

***In situ* electrochemical atomic force microscopy of
LiMn₂O₄ cathode in organic electrolyte**

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The development of surface structure-sensitive techniques in recent years has led to *in situ* electrochemical atomic force microscopy (EC-AFM), which provides useful information on surface chemistry, morphology, 3D structures, electrochemical response and performances of Li ion battery electrodes [1-7]. In this work, we studied *in situ* the surface of the spinel cathode with electrochemical atomic force microscopy (EC-AFM). We have also investigated the relationship between the morphological changes and the electrochemical characteristics.

The cathode material was prepared by mixing 75 wt % of LiMn₂O₄ (synthesized by Mitsubishi Chemical Corp.), 20 wt % of acetylene black (Denki Kagaku Kogyo Co. Ltd.), and 5 wt % of Teflon (Mitsui Dupont Fluoro Chemical Co. Ltd.) and the material was kneaded to a flat sheet with a mortar and a pestle. Before assembling the electrochemical cell, the working electrode was dried at 120°C in a vacuum oven for 2 hours. The electrolyte used for electrochemical measurements contained 1 mol of LiPF₆ in a mixed solvent of ethylene carbonate (EC), dimethyl carbonate (DMC), and diethyl carbonate (DEC) (2:2:1 by volume; Mitsubishi Chemical Corp.). The *in situ* EC-AFM observation was performed under potentiostatic conditions within 3.3 to 4.4 V using a Multimode AFM (NanoScope IIIA, Digital Instruments). Commercially available triangular gold-coated cantilevers with pyramidal tips with 0.05 N/m force constant were used. The electrochemical cell used in EC-AFM is similar to the cell used for other electrochemical measurements, e.g. it consists of cathode material as the working electrode and pure Li metal (Alfa Aesar) as the counter and reference electrode. All preparations and measurements were conducted at room temperature (25°C).

The *in situ* EC-AFM observation of the cathode surface was performed under potential control. At open circuit voltage, $E = 3.5\text{ V vs Li/Li}^+$, the surface is rough and movable material on the surface cause loss of resolution and produce streaking of the image. After one charge/discharge cycle the surface was cleaned up and no streaking of the image was observed. During the second charging process at 4.3 V vs Li/Li^+ , the dissolution of surface particles was observed. These particles were formed during the previous discharge process and show a crystalline morphology. Figure 1 shows the image of a surface particle during continuous scanning of which size gradually decreases and finally disappears, the dissolution rate following a power law in time as shown in Fig. 2.

During the second discharge process at 3.8 V vs Li/Li^+ , new particles are formed on the surface. However, after 3 min of scanning at 3.8 V there were no additional changes observed in the surface topography for another 20 min. The newly formed particles stopped growing after reaching a certain dimension. The observed surface dynamics suggest that a dissolution/precipitation reaction

is involved in the charge/discharge process of spinel LiMn₂O₄. Time elapsed EC-AFM studies were further correlated with the XPS data in order to clarify the surface reaction mechanism.

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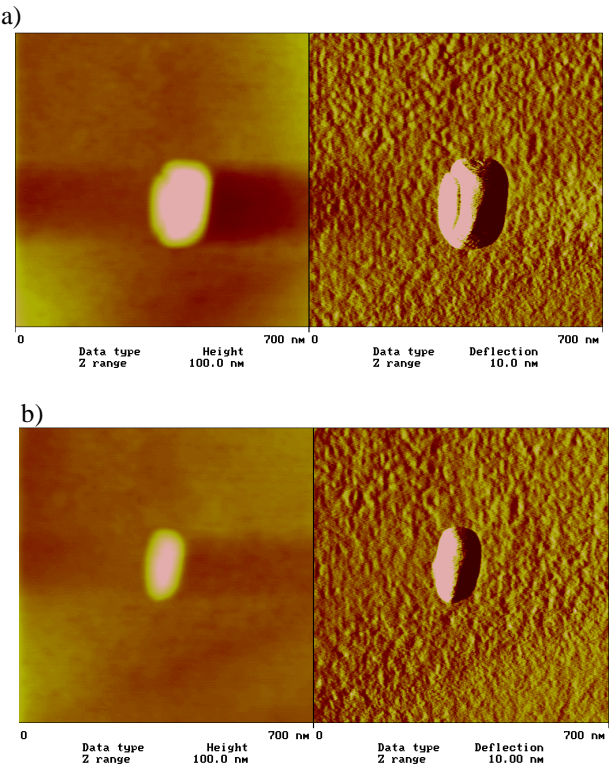


Figure 1. *In situ* EC-AFM image in height (left) and deflection (right) mode of surface particle dissolution at 4.3 V vs Li/Li^+ after 3 min (a) and 13 min (b).

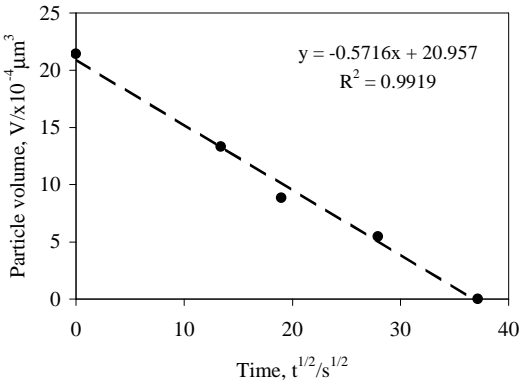


Figure 2. Dissolution rate of a surface particle.